Comment on "Semiconducting Layered Blue Phosphorus: A Computational Study"

Using results drawn from the pages of PRL[1], the authors comment on "Semiconducting Layered Blue Phosphorus: A Computational Study". In recent letter[1] unknown phase of phosphorus with high stability and a wide fundamental gap was proposed by Zhu, and Tománek. The first half of the comment questioned elements of phosphorus blue structure, while the second half devoted to van der Waals forces between AB stacked blue phosphorus layers which missed by them.

Converting a mono-layer of black to blue phosphorus, they used dislocation with constantlocal band angles and changed z lattice vector direction. This dislocation is not complete method for predicting new structure, While predicting a new system is available via *ab initio* evolutionary algorithm implemented for instance in USPEX code [2–4].

Using USPEX code accompanied with VASP [5], We found black phosphorous as the most stable structure and after that the blue phosphorous is stable with the difference energy of 2.62 eV. The interlayer distance, d_{int}, in above structure from USPEX prediction for Black and Blue ph. is 5.78 and 3.56 Å that is near to our results from ven der Waals calculation in table I. Then in monolayer structure, we found black monolayar is 0.034 eV stable than blue phosphorous monolayer.

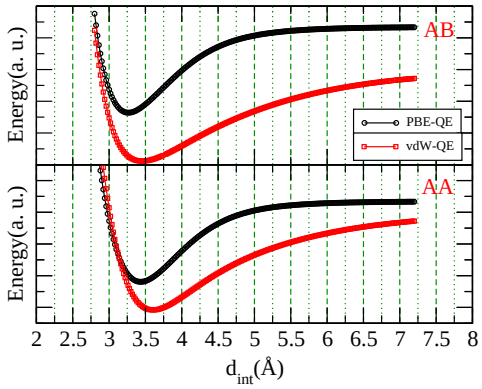

FIG. 1: Total interaction energy between two layer in AB and AA stacked blue phosphorous separated by the zero Å thick vacuum.

Presented here, reveals, the interlayer distance adopted in the letter are not in fact the most stable distance. The phosphorus layers, especially in blue configuration, stacked together by van der Waals interactions, like graphite[7].

The Brillouin zone of primitive cell for all calculation was sampled using 10×10×1 k points in standard DFT calculation pseudo-potential methods by Quantum Espresso (QE) (ecutwfc=40.0 and ecutrho=500) [6].

TABLE I: The nearest distance between the adjacent layer (d_{int}) interlayer distance for a, zero vacuum, and b, 15 Å vacuum,. $\Delta E^{'}$(Ry*10^{-2}) is, ΔE, energy difference between minimum energy level and straight energy level per atom. Values in parenthesis is related to black phosphorus.

name	a	a	b	b
	d_{int}(Å)	$\Delta E^{'}$	d_{int}(Å)	$\Delta E^{'}$
AB-PBE	3.26(5.40)	1.35(0.20)	3.06(5.82)	0.99(0.02)
AB-vdW-DF	3.46(5.62)	1.30(0.46)	3.12(5.86)	0.69(0.17)
AA-PBE	3.44(5.24)	1.26(0.39)	4.12(5.86)	0.10(0.03)
AA-vdW-DF	3.60(5.46)	1.40(0.59)	4.24(5.88)	0.32(0.18)

Concerning van der Waals (vdW) interaction via self consistent vdW-DF implemented in QE code, We found 3.46 and 3.12 Å as interlayer distance for two periodic array of AB stacked slab separated by a viz. a) zero and b)15 Å thick vacuum region, respectively. This distance is completely different of 5.63 angstrom mentioned in FIG. 1d of Letter [1]. In same calculation for AA stacked, d_{int} is 3.60 and 4.24 Å (see table I and figure 1). we repeated this calculation for black phosphorus, so interlayer distance reached its minimum in $\simeq$ 5.6 Å, in accordance with experimental results [7]. The difference between minimum energy level and straight energy level in black one is around 0.5*10^{-2} Ry, while in blue one is 1.30*10^{-2} Ry.

I. Abdolhosseini Sarsari[1], Z. Allahyari[1,2,3], M. Alaei[1] and S. Sanvito[4]
[1]Department of Physics, Isfahan University of Technology, Isfahan, 84156-83111, Iran
[2]Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, 141700, Russia
[3]Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, Bldg. 3, Moscow 143026, Russia
[4]School of Physics, AMBER and CRANN, Trinity College, Dublin 2, Ireland

[1] Zh. Zhu and D. Tománek, Phys. Rev. Lett. **112**, 176802 (2014).
[2] A. R. Oganov and C. W. Glass, J. Chem. Phys. **124**, 244704 (2006).
[3] C. W. Glass *et al.*, Comput. Phys. Commun. **175**, 713 (2006).
[4] Q. Zhu *et al.*, Phys. Rev. B **87**, 195317 (2013).
[5] M. Shishkin and G. Kresse, Phys. Rev. B **75**, 235102 (2007).
[6] P. Giannozzi *et al.*, Journal of Physics: Condensed Matter **39**, 395502 (19pp) (2009).
[7] Li. Likai *et al.*, Nature nanotechnology **9** 372 (2014).